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Microwave radiation induced synthesis of *Gum ghatti* and acrylamide based crosslinked network and evaluation of its thermal and electrical behavior

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ABSTRACT

Microwave radiation induced crosslinked network of Gum ghatti –acrylamide was synthesized using N, N'-methyene-bis-acrylamide (MBA) and potassium persulphate-ascorbic acid as a crosslinker-initiator system. Various reaction parameters like reaction time, amount of solvent, pH of medium, initiator ratio, microwave power, monomer and crosslinker concentrations were optimized so as to get the candidate polymer with maximum water absorption capacity (2010%). Effect of electrical field stimulus on the percentage deswelling of the candidate polymer was studied as a function of time of current flow and applied voltage. It was found that the candidate polymer exhibited maximum deswelling (57.47%) at 80V at a time interval of 6 min under the influence of DC field. Whereas, in case of AC electric field stimulus maximum percent deswelling (71.59%) was observed at 90V at a time interval of 6 min. Moreover, the crosslinked product was found to be thermally more stable than the backbone. Characterization was carried-out using different techniques like FTIR, SEM, XRD and TGA/DTA/DTG.

Keywords: *Gum ghatti*, acrylamide, crosslinked network, AC-DC stimuli, deswelling.

INTRODUCTION

Superabsorbent hydrogels are the materials which have three dimensional crosslinked network with excellent hydrophilic capacity [1, 2]. They can absorb water upto thousand folds of their initial weight and the swelled gel can retain water under even some pressure [3]. Carbohydrate polymers are often preferred over synthetic polymers due to their advantages like non-toxicity, low cost, ease of availability and biodegradable characteristics. Workers from all over the world are working on the graft copolymerization of different polysaccharides [4-9] and their potential applications in various fields like sustained drug delievery [10], waste water treatment [11,12], bio-medical applications and separation of saline water from different petroleum fraction-saline emulsions [13-15].

Stimuli-reponsive polymers are those which experience changes either in their structure or in their chemical properties under the influence of environmental conditions such as temperature, pH, light, electric field and certain chemicals [16, 17]. Osada *et al.* [18] reported the electrically activated artificial muscle system which contracted by the electrical stimulus under isothermal conditions. They reported that addition of NaCl increased the rate of water release whereas addition of organic solvents such as ethanol, acetone or water reduced the rate of water release and the contraction resulted from the electrostatic interaction between charged macromolecules and the electrodes lead extensive dehydration of the gel. Tanaka *et al.* [19] studied the effect of electric current on the contraction behavior of partially hydrolyzed polyacrylamide gels in a mixture of 50% acetone and water. They observed that the contraction was most significant and rapid in water while on increasing the acetone percentage rate of contraction decreased gradually. They explained the contraction phenomenon of gels on the basis of Flory-Higgins theory. Kim *et al.* [20] studied the effect of DC electric stimulus on the deswelling ratio and bending angle of polyelectrolyte complex composed of chitosan/hyaluronic acid in a solution of NaCl at different pH and observed that value of bending angle was less at very low and very high pH regions as compared to neutral pH. They suggested that low value of bending angle was due to the slow diffusion of ions from the crosslinked network in acidic and alkaline medium. Yang *et al.* [21] studied the effect of DC stimulus on polyelectrolyte gels as a function of deswelling and bending angle and concluded that in contact electric field deswelling at anode depends on field intensity whereas in non-contact electric field gel bend towards anode. Under the infuence of external stimuli such as pH, temperature and electric field hydrogels of polyacrylamide, partially hydrolysed acrylamide and their copolymers have been found to show a large volume changes [22-24].

In this research paper synthesis of *Gum ghatti*-acrylamide based hydrogels using KPS-ascorbic acid and N'N-methylene-bis-acrylamide as an initiator-crosslinker system under the influence of microwave radiations has been reported and effect of electrical stimulus on the deswelling of candidate polymer was studied with respect to time of current flow and applied.

MATERIALS AND METHODS

Gum ghatti (backbone) and potassium persulphate-ascorbic acid (initiator) procured from sd Fine Chemicals Pvt. Ltd., acrylamide (monomer) and N, N'-methylene-bis-acrylamide (crosslinker) purchased from MERCK were used as received.

Instrumental Analysis

FTIR analysis of the backbone and crosslinked product was carried-out on Perkin Elmer spectrophotometer using KBr pellets. Scanning Electron Micrographs of the candidate polymers were taken on LEO-435VF, LEO Electron Microscopy Ltd. Thermal studies (TGA/DTA/DTG) of the *Gum ghatti* and crosslinked Gg-cl-poly(AAm) were done on TG/DTA 6300, SII

EXSTAR 6000 in air at a heating rate of 10°C/min. X- Ray diffraction studies of the samples were carried-out on BRUKER AXS 08 ADVANCE.

Preparation of solutions of different pH

Alkaline solutions were prepared by the addition of NaOH pallets and acidic solutions were prepared by the addition of HCl using Cyberscan 1100, EUTECH INSTRUMENTS, pH meter.

Synthesis of superabsorbent

In a reaction flask *Gum ghatti* (1g) was added to the known volume of deionized water. A known molar ratio of ascorbic acid-KPS was also added to the reaction mixture and mixed thoroughly to attain the homogeneity. Functionalized polymer was crosslinked using N,N'-methylene-bis-acrylamide as a crosslinker. Different reaction parameters like reaction time, amount of solvent, pH of medium, microwave power and initiator ratio were optimized as a function of percentage grafting (P_g) as per the equation [13]:

$$P_g = \frac{W_f - W_b}{W_b} \text{ X } 100 \qquad (1)$$

where W_f and W_b are the weights of the functionalized polymer and backbone, respectively.

Acrylamide and MBA concentrations were optimized with respect to percent swelling as per the equation [13]:

$$P_s = \frac{W_s - W_d}{W_d} \text{ X } 100 \qquad (2)$$

where W_s and W_d are the weights of the swelled and dry polymer, respectively.

Electrical stimulus sensitive studies through DC/AC source

Apparatus used for the electrical stimulus sensitive studies is shown in Fig. 1. Preoptimized and dried hydrogel having weight (W_d) was immersed in deionized water for at least 2h and then was cut into rectangular shaped pieces with 10mm x 10mm x 5mm dimensions. Weight of the swollen gel (W_s) was taken and placed between two copper electrodes. Distance between two copper electrodes was about 5mm. On application of electrical stimulus water droplets started coming on the anodic side, which was removed with the help of light blotting tissue paper. Under the influence of electric field the gel began to deswell and was weighed after a regular time interval. Percentage deswelling (P_{ds}) was calculated by the formula:

$$\text{Percentage deswelling } (P_{ds}) = \frac{(W_s - W_d) - (W_{ds} - W_d)}{(W_s - W_d)} \text{ X } 100$$

where W_d and W_s are the weights of the dried and swelled samples respectively and W_{ds} is the weight of the sample after deswelling.

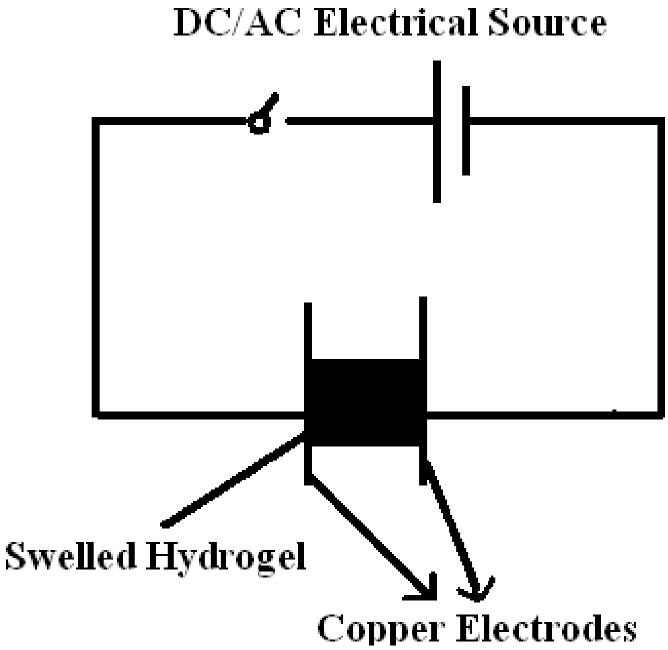


Fig. 1: Apparatus for AC/DC stimuli studies

RESULTS AND DISCUSSION

Mechanism

In case of natural polysaccharides hydroxyl groups (-OH) present on the backbone molecules are the active sites for the graft copolymerization. Various reactions involved in the graft copolymerization of *Gum ghatti*-acrylamide are depicted in Scheme-I.

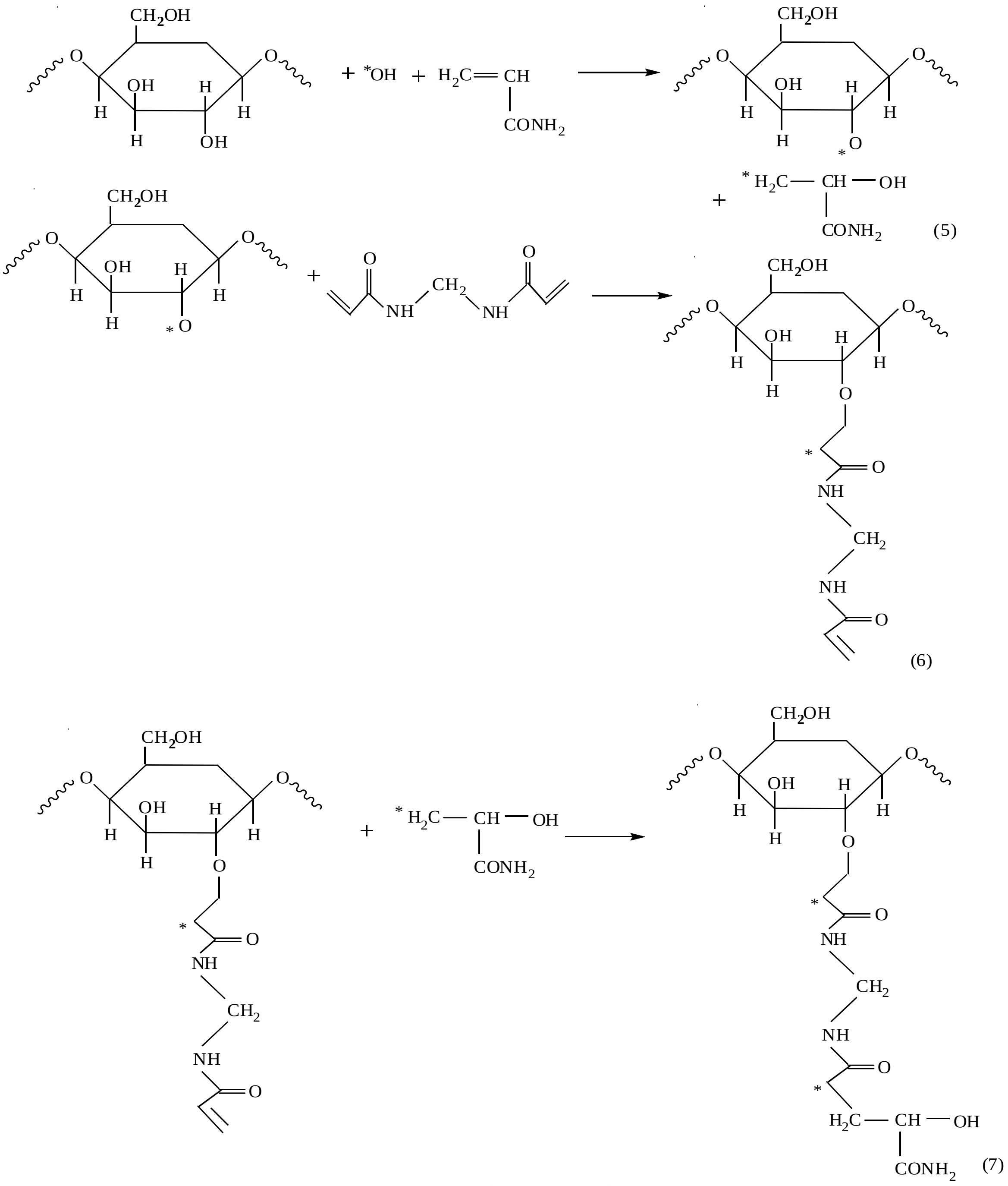
Initially, ascorbic acid reacts with persulphate to generate SO_4^{-*}(Eq. 3) which on further reaction with water molecules gives OH^* (Eq. 4). OH^* and SO_4^{-*} react with monomer and backbone molecules to produce free radical sites (Eq. 5). Activated monomer and backbone molecules propagate the molecular chain further and give rise to a crosslinked graft copolymer in presence of N, N'-methylene-bis-acrylamide (Eq. 7).

Optimization of various reaction parameters

The effect of reaction time on percentage grafting (P_g) is depicted in Fig. 2a. From the figure it is clear that maximum P_g (65%) was obtained at 90 seconds interval, whereas a decline in P_g was observed with further increase in reaction time which might be due to the fact that with the increase in reaction time homopolymerization predominates over graft copolymerization. Moreover, at higher time interval water soluble components of the backbone may go to the aqueous reaction medium, thereby reducing the P_g [13,14]. From Fig. 2b it is clear that optimized amount of solvent for maximum P_g (65%) was 10ml. Further increase in the amount of solvent resulted in decreased P_g which might be because of the fact that with the increase in amount of solvent concentration of OH^* decreases which further reduces the active sites generation on backbone and monomer moieties, hence decreased P_g was found. Maximum P_g (78%) was obtained at 0.5:1 molar ratio of ascorbic acid to KPS [Fig. 2c]. Initially P_g was found to increase with the increase in the molar ratio but after reaching maximum, a decline in P_g was observed which could be due to the fact that initially concentration of SO_4^{-*} (Eqs. 2-4, Scheme-I) and

$$ABC + S_2O_8^{2-} \longrightarrow SO_4^{-*} + DABC \qquad (3)$$

$$SO_4^{-*} + H_2O \longrightarrow HSO_4^{-} + {}^{*}OH \qquad (4)$$



Scheme I: Mechanism of synthesis of Gg-cl-poly(AAm)

ascorbic acid ion (III, Eq. 1, Scheme-I), get enhanced with the generation of more active sites and hence more P_g. However, further increase in the concentration of these ions resulted in chain termination reactions (Eq. 13-14, Scheme-I), which led to a deceased P_g. Fig. 2d showed the effect of microwave power on P_g. From the figure it is clear that maximum P_g (78%) was observed at 80%. Whereas, further increase in MWP resulted in decreased P_g, which might be due to the excessive homopolymerization or decomposition of grafted chain at higher MWP. It has been observed that optimum acrylamide concentration with respect to maximum P_s (2010%) in deionized water was 0.9859 molL^{-1} [Fig. 2e]. However, further increase in monomer concentration resulted in decreased P_s. It might be because of the fact that increase in monomer concentration beyond optimum level, leads to increase in inter- and intra-molecular self cross-linkage through secondary bonding forces with diminished porous gel structure which prevented the accessibility of more solvent into the polymeric matrix [25]. Maximum percent swelling (1974%) was reported at 0.081molL^{-1} of crosslinker concentration [Fig. 2f]. Further increase in the crosslinker concentration resulted in decreased P_s, because with the increase in crosslinker concentration cross-linking density increases thereby, leading to the decreased pore size and increased compactness. Hence lesser accommodation for solvent molecules was found.

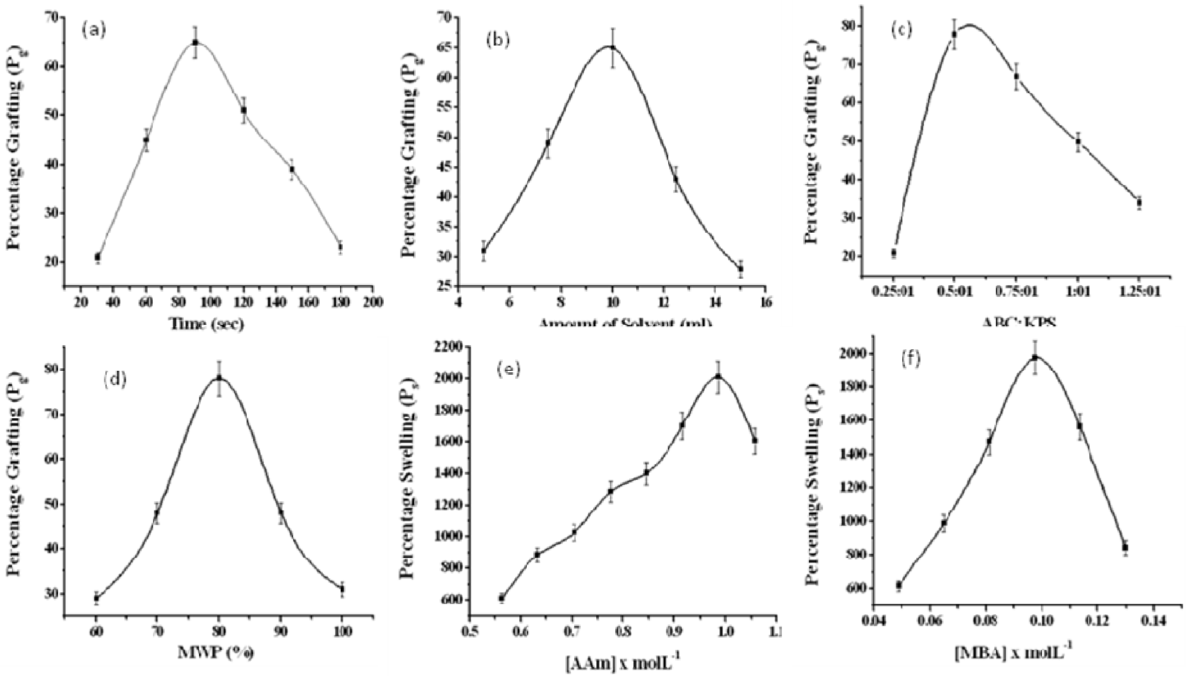


Fig. 2: (a) Effect of reaction time onto Percentage Grafting (P_g) Initiator ratio =1:1, [AAm]=0.7042molL^{-1} amount of solvent= 10ml; (b) Effect of amount of solvent onto percentage grafting [AAm]= 0.7042 molL^{-1}, reaction time = 90 sec, Initiator ratio = 1:1; (c) Effect of initiator ration on P_g [AAm]=0.7042 molL^{-1}, reaction time=90 sec, Initiator ratio=1:1; (d) Effect of microwave power onto P_g reaction time=90 sec, [AAm]=0.7042 molL^{-1}, amount of solvent=10ml; (e) Effect of con. of monomer onto P_s [MBA]=0.0649 molL^{-1}, initiator ratio=1:1, reaction time=90sec, amount of solvent=10ml; (f) Effect of con. of crosslinker onto Ps [AAm]=0.9859 molL^{-1}, reaction time=90 sec, amount of solvent=10ml, pH=7

Characterization

FTIR

In IR spectrum of *Gum ghatti* broad peak was observed at 3408.4 cm^{-1} due to -OH stretching of carbohydrates, peak at 2936.6 cm^{-1} was obtained because of -CH_2 asymmetric stretching. Peak at 643.71 cm^{-1} was because of pyranose ring. Whereas in case of Gg-cl-poly(AAm) peak at

2370.94 cm^{-1} was observed due to overtones and combination bands of –OH in plane bending and C-O stretching vibrations. Peak at 1645.26 cm^{-1} was because of C=O stretching of amide-I, peak at 1403.37 cm^{-1} was because of N-H in plane bending of amide-II, peak at 1103.50cm^{-1} was due to C-N stretching vibration of amide-III. Peak at 1019.54 cm^{-1} was because of C-O stretching of C=O group in addition to the peaks observed in the IR spectrum of *Gum ghatti*.

SEM

The morphology of *Gum ghatti* and Gg-cl-poly(AAm) were examined by SEM and presented in Fig. 3a and 3b, respectively. It was observed that *Gum ghatti* has smooth and homogeneous morphology whereas, Gg-cl-poly(AAm) has structural heterogeneity due to crosslinking with N, N'-methylene-bis-acrylamide.

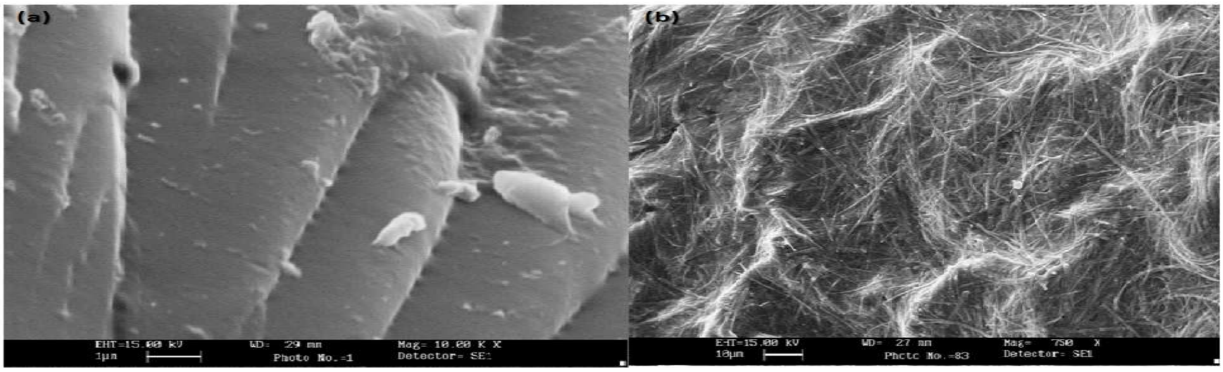


Fig. 3: SEM of (a) *Gum ghatti* (b) Gg-cl-poly(AAm)

Thermal studies

TGA of *Gum ghatti* as well as Gg-cl-poly(AAm) was carried-out as a function of percentage weight loss vs. temperature. In case of *Gum ghatti* two stage decomposition was observed in the temperature range from 212.1°-496.9°C with 65% weight loss and 496.6°-590°C with 35% weight loss. Whereas, in case of Gg-cl-poly(AAm)-MW first stage decomposition was observed from 152.3°-518°C with 57.7% weight loss and second stage decomposition was observed from 518°-611.8°C with 32.3% weight loss. First stage decomposition was due to initial dehydration and loss of volatile molecules whereas, second stage decomposition was due to depolymerization reactions. Initial decomposition temperature (IDT) of *Gum ghatti* (212.1°C) was higher than that of crosslinked polymer (152.3°C) while final decomposition temperature (FDT) of *Gum ghatti* (590°C) was lower than that of crosslinked product (611.8°C). It was observed that the difference in decomposition temperature for the crosslinked polymeric networks was more as compared to backbone, hence the rate of decomposition was slower in synthesized hydrogel. Further this might be because of the fact that crosslinked network exhibited more thermal stability because of the crosslinking of different polymeric chains [14]. These results were further supported by the data from DTA studies. Three exothermic peaks at 307.3°C (18.7µV), 331.8°C (21.1µV) and 496.9°C (238µV) corresponding to TGA temperature range of 212.1°-496.9°C and 496.9°-590°C, were obtained in case of *Gum ghatti*. Whereas, two exothermic peaks at 469.87°C (11.34 µV) and 596.3°C (155.1 µV) were obtained which corresponds to the TGA temperature range of 152.3°-518°C and 518°-611.8°C, respectively (Table 1). DTG studies were carried-out as a function of rate of weight loss (mg/min) versus temperature. In case of *Gum ghatti* decomposition at 245.4˚ and 488.9°C has been found with 0.625 and 1.875 mg/min weight loss, respectively. While in case of Gg-cl-poly(AAm) decomposition was observed at 216.9˚ and 595.9°C with 0.172 and 1.094 mg/min weight loss, respectively. Thus, from the DTG studies it is clear that the rate of thermal decomposition was higher in case of *Gum ghatti* in comparison to Gg-cl-poly(AAm). The better thermal resistance was due to incorporation of covalent bonds by the crosslinking between the different polymeric chains (Table 1).

X-Ray diffraction studies

From Table 2 it is clear that with increase in crosslinker concentration, d-spacing and coherence length decreases and also an increase in percent swelling was observed. Coherence length of the samples was calculated using the Schrerer equation [26, 27]:

$$L = 0.9\lambda / \beta_{1/2} \text{ x } \cos\theta$$

Where, λ=wavelength, θ=diffraction angle, L=coherence length and $\beta_{1/2}$=full width half maximum.

It is observed from the Table 2 that in case of Gg-cl-poly(AAm)-MW, the crosslinked polymers with crosslinker concentration 0.0487, 0.0649, 0.0810, 0.0974 and 0.1136 $molL^{-1}$ maximum intensity peak corresponds to 2θ=24.971° (L=1.668 Å), 24.428° (L=1.744 Å), 22.739° (L=1.815 Å), 20.666° (L=1.853 Å) and 19.567° (L=1.976 Å), respectively. Coherence length as found to increase with increase in crosslinker concentration leading to the increased anisotropy and the polymer became more crystalline in nature. This might be due to the fact that with increase in crosslinker concentration, crosslinking density between polymeric chains got enhanced leading to more aligned crystalline structure.

Table 1: Thermal behavior of *Gum ghatti* and Gg-cl-poly(AAm)

Sample Code	**TGA**				**DTA**			**DTG**	
	IDT (^{0}C)	**1st stage Decomposition, ^{0}C (% wt. loss)**	**2nd stage Decomposition, ^{0}C (% wt. loss)**	**FDT, ^{0}C (residue left)**	**Exothermic peaks at different decomposition Temperature (µV)**			**Decomposition Temperature ˚C (Rate of wt. loss in mg/min)**	
					1st (˚C)	**2nd (˚C)**	**3rd ˚C)**	**1st (˚C)**	**2nd (˚C)**
Gum Ghatti	212.1	212.1-496.9 (65%)	496.6-590 (32.5%)	590 (0.00)	307.3 (18.7)	331.8 (21.1)	496.9 (23.8)	245.4 (0.625)	488.9 (1.875)
Gg-cl-poly(AAm)	152.3	152.3-518 (57.7%)	518°-611.8 (32.3)	611.8 2.5%)	469.87 (11.34)	596.3 (155.1)	-	382.3 (0.393)	594.5 (0.873)

where IDT=Initial decomposition temperature, FDT=Final decomposition temperature, TGA=Thermo gravimetric analysis, DTA=Differential thermal analysis, DTG=Differential thermo gravimetric analysis and Gg-cl-poly(AAm)=Crossslinked graft copolymer of acrylamide onto Gum ghatti.

Table 2: Effect of concentration of crosslinker on d-spacing and coherence length

Sample Code	Crosslinker ($molL^{-1}$)	d-Spacing	Angle of Diffraction at 2Θ-scale	FWHM at 2Θ- scale	Coherence length (Å)
Gg		4.24532	20.908°	13.17°	1.057
Gg-cl-poly(AAm)-I	0.0487	3.5608	24.971°	8.2305°	1.668
Gg-cl-poly(AAm)-II	0.0649	3.6410	24.428°	7.8696°	1.744
Gg-cl-poly(AAm)-III	0.0810	3.9014	22.739°	7.5586°	1.815
Gg-cl-poly(AAm)-IV	0.0974	4.2944	20.666°	7.4059°	1.853
Gg-cl-poly(AAm)-V	0.1136	4.5330	19.567°	6.9365°	1.976

where Gg=Gum ghatti, P_g=Percentage grafting, P_s=Percentage swelling, FWHM=Full width half maximum

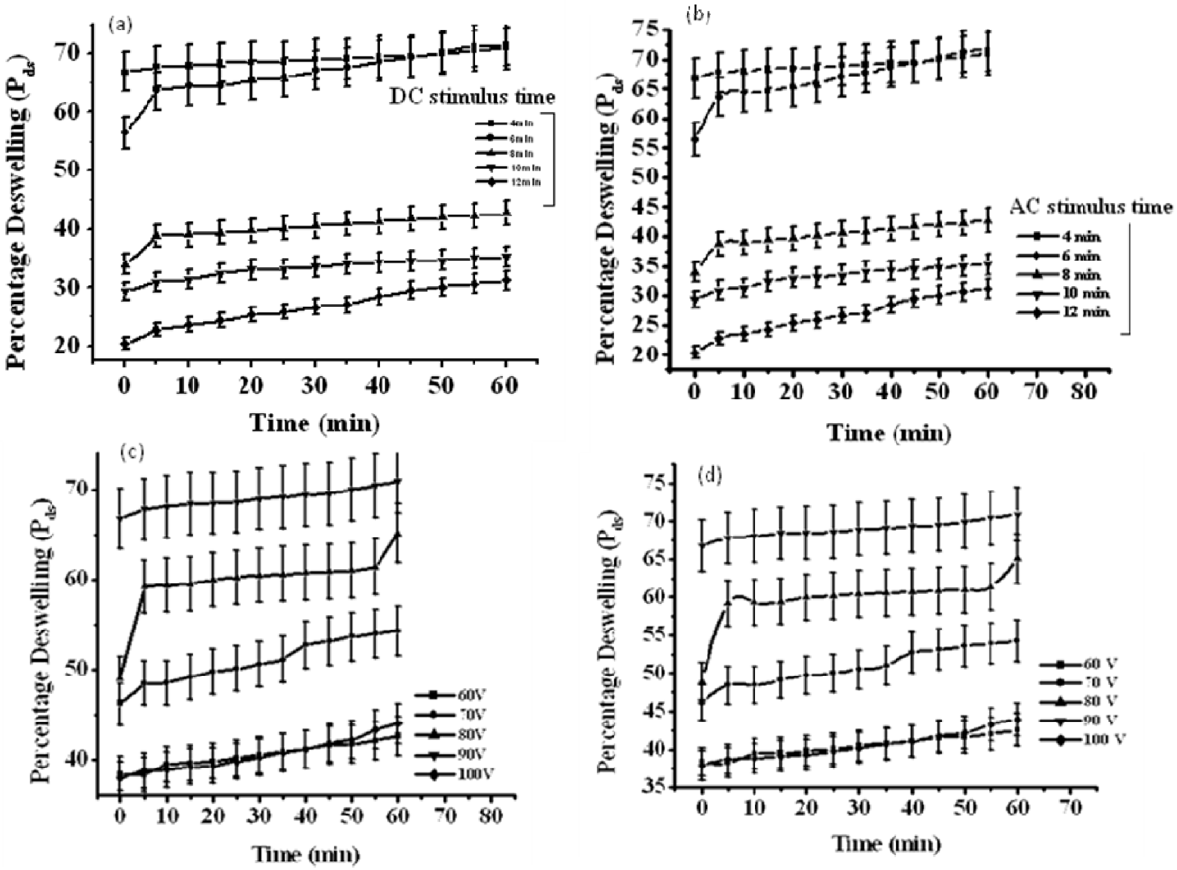


Fig. 4: (a) Effect of DC stimulus time on percent deswelling; (b) Effect of AC stimulus time on percent deswelling; (c) Effect of applied voltage on percent deswelling in DC stimulus field; (d) Effect of applied voltage on percent deswelling in AC stimulus field

Electrical stimulus sensitive studies through DC/AC source

Effect of time of current flow

From Figs. 4a-b it is clear that initially rate of removal of water molecules from the gel network was higher, which kept on decreasing slowly. In case of both AC and DC stimuli the optimized time for maximum deswelling was observed to be 6 min. Further increase in the time of DC/AC stimulus percentage deswelling was found to decrease which might be because of the fact that further DC/AC stimulus time resulted in electrolysis of water content imbibed within the network polymer into H^+ and OH^- ions. Though most of the H^+ and OH^- ions being smaller in size easily make their way out of the gel but remaining ions exert an ion screening effect within the gel thereby leading to decreased deswelling. Moreover, further increase in electrical stimulus time resulted in the production of more concentration of H^+ and OH^- ions and increase in electrostatic repulsion between the H^+/H^+ and OH^-/OH^- ions and hence decreased percent deswelling was observed.

Effect of applied voltage

Water release studies of the gels were carried out with the application of the DC/AC electric field stimulus at different voltages (60, 70, 80, 90 and 100V). It was found that initially with the increase in the applied voltage percentage deswelling increases but after getting optimized voltage (80V in case DC slimulus and 90V in case of AC stimulus) percentage deswelling decreases (Figs. 4c-d). Which could be because of the fact that though initially with increase in voltage the speed of transfer of H^+ and OH^- ions toward the opposite electrodes increases and there is an easy escape of these ions out of the gel and consequently there is increased deswelling rate but with further increase in the voltage, due to electrolysis there is more generation of H^+ and OH^- ions which exerted ion screening effect due to electrostatic repulsions and resulted in the decreased rate of shrinkage of crosslinked system.

CONCLUSION

From the ongoing studies it is observed that methylene-bis-acrylamide crosslinked network obtained from acrylamide and *Gum ghatti* is thermally more stable than the backbone. Moreover, the synthesized polymer was found to exhibit deswelling sensitivity towards AC and DC electric stimuli which further was found to be stimulus time, applied voltage and pH dependent. Thus, the synthesized candidate polymer is of great significance from technology view point.

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